Use of Surface Chemkin to Model Multiphase Atmospheric Chemistry: Application to Nitrogen Tetroxide Spills

27 March 2000

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VICE PRESIDENT
Laboratory Operations

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USE OF SURFACE CHEMKIN TO MODEL MULTIPHASE ATMOSPHERIC CHEMISTRY: APPLICATION TO NITROGEN TETROXIDE SPILLS

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Contract No. F04701-93-C-0094
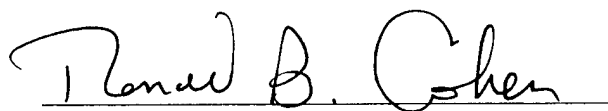
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1352-2310(94)00304-1

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Abstract—SURFACE CHEMKIN is a widely available* computer program developed for kinetic modeling of chemical vapor deposition. We show that it may be adapted for kinetic modeling of multiphase chemistry in the atmosphere, with broad capability to deal with complex chemistry and physics. It can deal with multiple phases having different reaction manifolds in each phase, it deals with gas, surface, and bulk reactions and mass transfer rates, it keeps track of the phase equilibria with realistic activities, and it can operate in an adiabatic mode to include the effect of heat release on the system. The adapted model is applied here to the problem of a nitrogen tetroxide spill in the troposphere. The model is able to predict the formation of a nitric acid/water aerosol and to follow the chemistry taking place in both the gas and liquid phases as the spill dilutes in the surrounding atmosphere. The model predicts that in such a spill, most (70–90%) of the nitrogen oxides released are converted to nitric acid over a wide range of relative humidity.

Key word index: Heterogeneous chemistry, kinetics, dispersion, toxic plume.

INTRODUCTION

The importance of heterogeneous or multiphase chemistry in the atmosphere has only recently been recognized. Chemistry in the aqueous phase of cloud drops was shown to be important in the atmospheric transformation and transport of sulfur in connection with acid rain in the early 1980s (Martin, 1984; Oppenheimer, 1983; Daum *et al.*, 1984). Surface chemistry on polar stratospheric clouds has been shown to be of key importance in explaining the Antarctic ozone hole (McElroy and Salawitch, 1989; McElroy *et al.*, 1986; Solomon *et al.*, 1986). Surface chemistry has also been shown to be important in the NO_y chemistry of the troposphere (Heikes and Thompson, 1983) and in the mid-latitude stratosphere (Brasseur *et al.*, 1990; Granier and Brasseur, 1992).

Multiphase chemistry poses special problems in computer kinetic modeling for a number of reasons. (1) Chemical reactions on or within the second phase will in general have different rates from those in the gas phase, so more than one manifold of rate constants may be required. (2) Mass transfer to or within the second phase may be rate limiting, rather than

chemical kinetics. (3) The formation of a condensed phase usually involves a discontinuity in the activity of a species, which is difficult for computer programs to handle. (4) The formation of a condensed phase will in general release a great deal of heat. (5) Concentrated spills of certain gases such as HCl cause aerosol formation because they reduce the partial pressure of water of the liquid phase, thus permitting liquid to exist at less than 100% humidity (deliquescence). In such cases, the amount of liquid phase present will be strongly coupled to the progress of the chemical reactions.

An atmospheric release of nitrogen tetroxide involves all of these problems. Upon release, the following sequence of events will take place: first, there is rapid but incomplete dissociation of the nitrogen tetroxide (N_2O_4) to form nitrogen dioxide (NO_2). Both the dioxide and the tetroxide react at different rates with small amounts of water adsorbed on the surface of naturally occurring aerosols, leading to the formation of nitric acid, which is deliquescent. Water vapor in the ambient air will condense in the nitric acid, producing a liquid phase in increasing amounts. This liquid phase is a more favorable medium for chemical reactions between the oxides of nitrogen and water, so the entire process will accelerate. Thus, a cloud will grow by this "bootstrap" process. As all of this happens, the heat released by condensation and by exothermic reactions will increase the temperature of the air parcel, and this in turn may limit the formation

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of liquid. Modeling this complex process is a challenge.

Several models have appeared in the literature which deal with various aspects of the multiphase problem. A fog chemistry model by Pilinis et al. (1992) includes multiphase chemistry and equilibria as well as aerosol dynamics, mass transfer rates and wet and dry deposition. Thermal effects and mixing with the surrounding atmosphere are not included, so the model was not designed to deal with the unusual situation of a concentrated nitrogen oxide spill, in which the effects of heat release and dilution cannot be ignored. A model by Moller and Mauersberger (1992) deals with both liquid and gas-phase chemistry, but is constrained to a fixed droplet size. Spill models by Balentine and Eltgroth (1985), Spicer and Havens (1987), Spicer et al. (1986) and Lyons et al. (1990) deal with the physics but not the chemistry of the dispersing material. A model by Rodean (1989, 1991) and the ADAM model (Raj and Morris, 1987; Mullet and Raj, 1990) deal with the formation of nitric acid from a nitrogen tetroxide spill, but these models are based on thermodynamics and not kinetics. A model by Cho et al. (1992) includes detailed multiphase chemistry and physics as well as thermal effects, but is designed to look primarily at the microphysics of individual particles or droplets.

In this paper, we show that a recently developed computer chemical kinetics program can be modified in a straightforward way to deal with the problem of a concentrated spill. The program is SURFACE CHEMKIN, developed by Robert Kee of Sandia, Livermore, and available from the laboratory via licensing agreements (Coltrin et al., 1991; Kee et al., 1991a,b). The program was developed to model chemical vapor deposition, but lends itself to complex atmospheric chemistry problems. It is capable of dealing with multiple phases, with different reaction manifolds in each phase; it deals with gas, surface, and bulk reactions and mass transfer rates; it keeps track of the phase equilibria with realistic activities; and it can operate in an adiabatic mode to include the effect of heat release on the system. The effects of dilution of a spill with time can also be included.

We have applied this program to the problem of a large spill of nitrogen tetroxide in the atmosphere. This problem involves all of the complexities described above, because of the unique properties of the nitrogen oxide–water system. Nitrogen oxide spills are a potential hazard from the storage and handling of rocket oxidizer (Watje, 1978; Haas and Prince, 1984), and experiments have been conducted on the release of nitrogen oxides into the troposphere (McRae, 1985; McRae et al., 1984, 1987).

MODEL DESCRIPTION

The computer model is based on the SURFACE CHEM-KIN code developed by R. J. Kee of Sandia, Livermore. This package contains subroutines for calculating thermodynamic properties, equilibrium constants, rates, and unit conversions, for parsing character data such as species and element names, and reaction mechanisms, and for solving the set of differential equations. SURFACE CHEMKIN is a set of software tools and a subroutine library designed to help create a program to solve a specific chemical kinetics problem. The package is designed to solve a group of differential equations subject to a set of constraints; various properties of the system may be extracted along the way. One needs to write the program which describes the chemical system of interest, and calls the appropriate subroutines to do the calculations. Multiple surface and bulk phases can be included. Surface rates are scaled by the ratio of surface area to gas-phase volume. The package is designed to model chemical vapor deposition. We wrote a driver program incorporating some changes in the calculation method, added some new subroutines, and modified some of the original routines. The resulting program is well adapted to atmospheric chemistry. Our alterations are described in more detail below.

The plume model is adiabatic. Chemkin calculates the enthalpy of each species in the model. As species are created or destroyed through reaction they add or subtract energy from the plume; mixing with the air also effects the energy balance. This net change in energy is divided by the heat capacity of the plume to obtain the temperature change for each integration step. This energy conservation equation is included as a governing equation, or constraint, for SURFACE CHEMKIN.

The governing equation for temperature, alluded to above, is based on conservation of energy, and is included here for reference:

$$\frac{\partial T}{\partial t} = \frac{\sum_{i=1}^{N} H_i^m m_i \left[\frac{\partial n_i^g}{\partial t} + \frac{\partial n_i^s}{\partial t} A_R + \frac{\partial n_i^l}{\partial t} V_R \right] + (T^{Air} - T) \frac{\partial \sigma_p}{\sigma_p \partial t} C_p^{air}}{(C_p^g \rho + C_p' m_l)}.$$

The preceding equation describes the change in the plume temperature with time. The numerator in this equation is the total enthalpy change for the plume in time interval ∂t. The summation is over species i, where N is the total number of species considered; here N is 25. H_i^m is the enthalpy in mass units, m_i is the molecular weight of species i, and n_i^{phase} is the number of moles produced by gas, g, surface, s, or liquid phase, l, reactions per unit volume (area for phase = s); the product $H_i^m m_i \partial n_i^g / \partial t$ represents the heat gained or lost to the plume due to the production (or consumption) of a particular chemical species in gas-phase reactions in the time interval ∂t. The rate of species production from surface reactions, $\partial n_i^s / \partial t$ is normalized by A_R, the ratio of surface area to gas-phase volume. V_R is the ratio of liquid-phase volume to gas-phase volume, which normalizes the rate of species production from bulk phase reactions, $\partial n_i^l / \partial t$. T is the temperature. σ_p is the cross-sectional area of the plume, and C_p is heat capacity. The term $(T^{air} - T) \partial \sigma_p / \sigma_p \partial t \, C_p^{air}$ represents the heat required to bring ambient air, which is mixing into the plume, to the same temperature as the plume gases. The superscript air refers to quantities in the undisturbed air outside the plume. The denominator in the above equation represents the specific heat of the plume and is made up of the specific heat of the gas phase, $C_p^g \rho$, and condensed phase, $C_p' m_l$, portions, where ρ is the gas-phase density, and the total mass in the liquid phase per unit volume of gas is m_l. The heat capacity of the surface phase is negligible and is ignored.

The remaining constraints are based on conservation of mass and are broken down into separate equations for each species in each phase. The governing equation for gas-phase

species is

$$\frac{\partial Y_i}{\partial t} = \frac{m_i}{\rho}\left[\frac{\partial n_i^g}{\partial t} + \frac{\partial n_i^s}{\partial t}A_R + \frac{\partial n_i'}{\partial t}V_R\right] + (Y_i^{air} - Y_i^g)\frac{\partial\sigma_p}{\sigma_p\partial t}.$$

The symbol Y is used for the gas-phase mass fraction. The first term in this equation is the molar changes due to reaction converted to a mass fraction, and the second term is the effect of dilution on plume species. This equation has a similar structure to the numerator of the first governing equation.

The equation for surface species in terms of site fraction, X_j, is similar. There is also a correction for coverage, where the density of surface sites in a given surface phase j is given by Γ_j and the number of sites occupied by a given species is σ_i. Large molecules could occupy several sites, but all the species in this model are small molecules with $\sigma_i = 1$. Only one surface phase is used in our model. There is an equation like the following one for each surface species:

$$\frac{\partial X_i}{\partial t} = \left(\frac{\partial n_i^s}{\partial t} + \frac{\partial n_i'}{\partial t}V_R\right)\frac{\sigma_i}{\Gamma_j}.$$

The equations for liquid species are also similar, but given in mass, z_j. A term for dry deposition is added. Multiple bulk phases are possible, but only one is used here. An equation like the following is generated for each species in the liquid phase.

$$\frac{\partial z_i}{\partial t} = m_i\left[\frac{\partial n_i^s}{\partial t}A_R + \frac{\partial n_i'}{\partial t}V_R\right] + (z_i^{air} - z_i')\frac{\partial\sigma_p}{\sigma_p\partial t}$$
$$- z_i'[\sigma_z(0)/\sigma_z(t)]^{v_d\sqrt{2/\pi}/au}$$

where the final term is an approximate correction for dry deposition described below. This complete set of constraints is used in solving the differential equations from the kinetics for each time step in the simulation.

We have made several changes to the Sandia package. To model an aerosol we keep track of the total condensed volume and let the surface area vary with the volume and droplet size. We created a separate set of pure bulk phase (non-surface) reactions whose rates are scaled by the ratio of condensed phase volume to gas volume. We also needed to add the effect of atmospheric dispersion. For purposes of this demonstration, we use a simple Gaussian plume model, and we consider only the centerline concentration:

$$C^0 = \frac{R}{v}\left(\frac{1}{\pi\sigma_y\sigma_z}\right)$$

where R is the evaporation rate of N_2O_4, v is the wind speed, and s_y and s_z are the plume spreading parameters for the horizontal and vertical directions. For simplicity, the spreading parameters, σ_y and σ_z, are taken to increase linearly with time: $\sigma_z = \sigma_z(0) + ax$; $\sigma_y(0) + bx$; for this case, $\sigma_z = 1 + 0.07x$ (m) and $\sigma_y = 2 + 0.10x$ (m), which corresponds roughly to the Pasquill stability class "C"; this essentially means that in the absence of reactions, the concentration drops with the square of time. The time derivative of this equation is included in the model. More sophisticated dispersion models are available, but the purpose of this test was primarily to see the effect of the aerosol chemistry.

A second set of initial conditions is used for the atmospheric temperature and composition; background atmospheric gases in the plume increase at the same rate the plume gases decrease. The total pressure is conserved. The program was run at this point with a helium tracer added to the initial plume. The helium mole fraction is always less than 1% and thus does not appreciably alter the density of the plume. The helium does not participate in reactions, therefore its concentration decreases strictly with the square of time. This allowed us to test separately the effects of reaction and dilution. Conservation of mass requires that the

sum of all moles of nitrogen oxides in all phases divided by the moles of helium be a constant:

$$\frac{\sum\limits_{p=g,s,aq} n_{NO}^p + n_{NO_2}^p + 2n_{N_2O_4}^p + n_{HNO_2}^p + n_{HNO_3}^p}{n_{He}^g} = C_1.$$

Two more changes have been added to the program. Approximate corrections for dry deposition of aerosol and for photolysis rates are included. For dry deposition, we make the following correction to the concentrations, based on the source depletion model (Overcamp, 1976; Horst, 1977; Corbett, 1981):

$$C = C_0[\sigma_z(0)/\sigma_z(t)]^{v_d\sqrt{2/\pi}/au}$$

where v_d is the deposition velocity, a is the coefficient of x in the expression for σ_z as shown above, and u is the wind speed. A nominal dry deposition velocity of $1\,\text{cm s}^{-1}$ ($0.01\,\text{M s}^{-1}$) is chosen for NO_2 (McRae and Russell, 1984) and for HNO_3 (Huebert and Robert, 1985) and for the liquid droplets, since the settling velocity for the model calculated droplets is also roughly $1\,\text{cm s}^{-1}$. Photolysis rates are entered as the average daytime rate. Since the plume is at first optically thick, the overall photolysis rate was approximated by multiplying by I/I_0, where

$$I/I_0 = 10^{aP\sigma_z}.$$

Little difference in the final results was seen with I/I_0 equal to 0 or 1, so this approximation of reduced but uniform photolysis is not critical: The adsorption constant for NO_2, a, was taken as $15\,\text{cm}^{-1}\,\text{atm}^{-1}$; P is the pressure of NO_2.

The bulk-phase activity coefficients were set equal to the liquid mole fraction with two exceptions. Water and nitric acid form an azeotrope; the real activity coefficients for these species were fitted to a quadratic equation in the mole fraction and this equation was used in the program. Thermodynamic data for the bulk species not available in SURFACE CHEMKIN were taken from the JANAF Thermochemical Tables (Chase, 1985) and The International Critical Tables (National Research Council, 1928); surface species are assumed to have the same properties as bulk phase species for this simulation. The temperature dependence of the gas-phase rates is included.

MODEL TESTS

Our first test of the model involved simple condensation. We created a hypothetical gas-phase reaction that ran at room temperature and had water vapor as a product. The model correctly determined that the gas-phase water concentration increased until it reached the equilibrium vapor pressure, at which point liquid water began to form. A temporary overshoot in the water vapor pressure could occur if the initial reaction rate was much faster than the rate of condensation.

A second test of the program was for the case of constant liquid to gas volume ratio and constant droplet size because we were able to solve this case with a hand calculation. We let dissolved NO_2 react with liquid water,

$$2NO_{2(aq)} + H_2O_{(1)} \xrightarrow{k} HNO_{3(aq)} + HNO_{2(aq)}$$
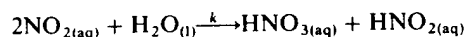
but set the rate for evaporation or condensation of the water to zero. The half-life of the NO_2 is calculated in

this case as

$$t_{1/2} = \frac{1}{(2K'C_g^0)}$$

where

$$K' = \frac{kV_R H^2}{(1 + V_R H)}.$$

The quantity, V_R, is the ratio of the liquid-phase volume to gas-phase volume, H is the Henry's law constant for NO_2 in water, C_g^0 is the initial gas-phase concentration of NO_2, and k is the reaction rate constant. We also checked the mass balance to insure that there was no net loss or creation of material. For atmospheric reactions the pressure is held constant.

The model was constructed to simulate the effects of an accidental release or spill of liquid nitrogen tetroxide, N_2O_4, or NTO, which is used as a rocket propellant in large launch vehicles. The initial plume from the spill is assumed to be 99% gaseous NTO and 1% helium. The helium is for diagnostic purposes as explained earlier. The effluent expands and mixes with air in accordance with a Gaussian model. The wind speed is 10 km h^{-1} and the dispersion is an intermediate case. The background air is made up of nitrogen and oxygen in the usual abundances, 20 ppb nitrogen dioxide, and water vapor varying with the humidity. The background air is also assumed to contain a marine aerosol, 0.2 ppbv, half a micron in diameter, and consisting of water and sodium chloride. Such an aerosol is typical at coastal sites, such as Cape Canaveral and Vandenberg Air Force Base. The proportions of water and salt in the aerosol vary with the humidity. For simplicity, aerosol particles are also assumed to be present in the initial NTO plume. The

simulation was run at 1 atm pressure and 293 K for 1 h.

The reaction mechanism includes 12 gas-phase reactions, 11 surface reactions, and two bulk-phase reactions and is illustrated schematically in Fig. 1. In this figure the boxes represent species within a specified phase. Arrows connecting the boxes represent chemical reactions or mass transport paths connecting the species, with the principle reactants indicated beside the arrows. A complete list of the reactions and rate constants are listed in Table 1. Mass transport between phases in handled via surface reactions. Mass transport is assumed not to be rate limiting except for the case of reaction of N_2O_4 with the droplet surface, as discussed below. Using a formula for the characteristic time for macroscopic mass transport (interstitial gas-to-droplet diffusion) developed by Schwartz (1984) (Levine and Schwartz, 1982):

$$\tau_{(mt)} = (12D_g L \langle D^{-2} \rangle)^{-1}$$

where D_g is gas-phase diffusivity, L is liquid volume fraction, and D is the droplet diameter. For our calculated cloud properties, we get a characteristic time of about 0.1 s. Since the model results without mass transport limitation show that most of the aerosol chemical reactions take place on a scale of about 10 s, macroscopic mass transport should not be a limitation.

The rates of the gas-phase reactions are taken from the NIST Database (1992), and the aqueous phase rates from Park and Lee (1988). The decomposition of nitrous acid has been proposed to be a surface reaction by Kobayashi et al. (1976), and the program could easily incorporate this kind of reaction if the surface reaction rate could be quantified. For the
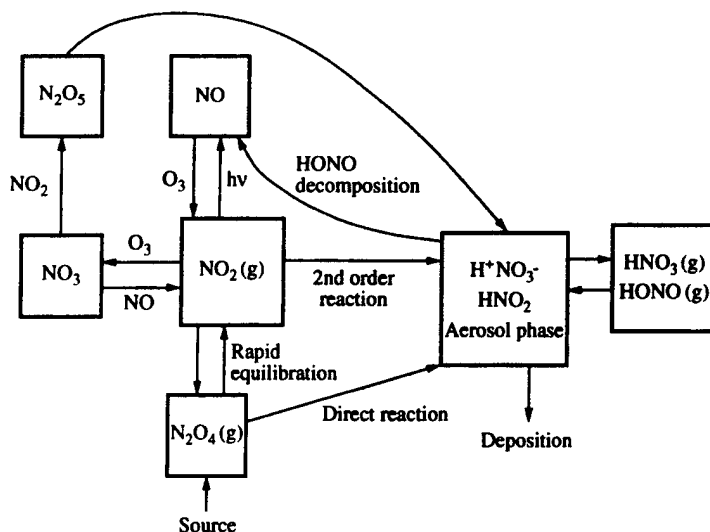

Fig. 1. Schematic diagram of the main chemistry. The boxes represent species within a specified phase. Arrows connecting the boxes represent chemical reactions or mass transport paths connecting the species, with the principle reactants indicated beside the arrows. A complete list of reactions is given in Table 1.

Table 1. Reaction mechanism

Reactions	Rates
Gas phase	
$O_3 + NO_2 \rightleftharpoons NO_3 + O_2$	$1.14 \times 10^{11} e^{-2542/T}$
$O + NO_2 \rightleftharpoons O_2 + NO$	$3.98 \times 10^{12} e^{90/T}$
$O + NO_2 + M \rightleftharpoons NO_3 + M$	$5.32 \times 10^{15} e^{532/T}$
$O + O_2 + M \rightleftharpoons O_3 + M$	$3.35 \times 10^{13} e^{489/T}$
$OH + NO_2 + M \rightleftharpoons HNO_3 + M$	$3.04 \times 10^{1} e^{918/T}$
$NO + NO_3 \rightleftharpoons 2NO_2$	$6.32 \times 10^{12} e^{223/T}$
$NO + O_3 \rightleftharpoons NO_2 + O_2$	$1.47 \times 10^{12} e^{-1446/T}$
$NO_2 + NO_3 + M \rightleftharpoons N_2O_5 + M$	$2.86 \times 10^{16} e^{1062/T}$
$N_2O_5 \rightleftharpoons NO_2 + NO_3$	$1.59 \times 10^{15} e^{-11223/T}$
$N_2O_4 + M \rightleftharpoons 2NO_2 + M$	$1.46 \times 10^{17} e^{-5314/T}$
$2HONO \rightleftharpoons NO_2 + NO + H_2O$	$1.00 \times 10^{13} e^{-4292/T}$
$2NO + O_2 \rightleftharpoons 2NO_2$	1.45×10^{10}
Surface	
$N_2O_{4(g)} + H_2O_{(surf)} \rightleftharpoons HNO_{3(aq)} + HONO_{(surf)}$	$0.001 \leqslant \gamma \leqslant 1$
$N_2O_{5(g)} + H_2O_{(surf)} \rightleftharpoons HNO_{3(aq)} + HNO_{3(surf)}$	$\gamma = 1$
Bulk	
$2NO_{2(aq)} + H_2O_{(l)} \rightleftharpoons HNO_{3(aq)} + HONO_{(aq)}$	8.4×10^{10}
$HONO_{(aq)} + HONO_{(aq)} \rightleftharpoons NO_{2(aq)} + NO_{(g)} + H_2O_{(aq)}$	1.3×10^{4}
Mass transport	
$H_2O_{(g)} + H_2O_{(surf)} \rightleftharpoons H_2O_{(surf)} + H_2O_{(l)}$	$\gamma = 1$
$H_2O_{(g)} + NaCl_{(surf)} \rightleftharpoons H_2O_{(surf)} + NaCl_{(sq)}$	$\gamma = 1$
$NO_{2(g)} + H_2O_{(surf)} \rightleftharpoons NO_{2(aq)} + H_2O_{(surf)}$	$\gamma = 1$
$NO_{(g)} + H_2O_{(surf)} \rightleftharpoons NO_{(aq)} + H_2O_{(surf)}$	$\gamma = 1$
$HNO_{3(g)} + H_2O_{(surf)} \rightleftharpoons HNO_{3(surf)} + H_2O_{(l)}$	$\gamma = 1$
$HONO_{(g)} + H_2O_{(surf)} \rightleftharpoons HONO_{(surf)} + H_2O_{(l)}$	$\gamma = 1$
$HNO_{3(surf)} + H_2O_{(l)} \rightleftharpoons H_2O_{(surf)} + HNO_{3(aq)}$	1.0×10^{10}
$HONO_{(surf)} + H_2O_{(l)} \rightleftharpoons H_2O_{(surf)} + HONO_{(aq)}$	1.0×10^{10}
$NaCl_{(surf)} + H_2O_{(l)} \rightleftharpoons NaCl_{(aq)} + H_2O_{(surf)}$	1.0×10^{10}

Note: Gas-phase reaction rates are in units of $cm^3 mol^{-1} s^{-1}$ for two-body reactions and $cm^6 mol^{-2} s^{-1}$ for three-body reactions. The liquid-phase rates are in $cm^3 mol^{-1} s^{-1}$ and must be multiplied by $(0.0555)^2$ to be used correctly by the the program. All gas-phase rates are from NIST (1992) and the liquid-phase rates from Park and Lee (1988). The gas-surface reactions and the surface-bulk reactions are taken not to be rate limiting except for the N_2O_4 + water reaction, as described in the text. T is the temperature, γ is the sticking coefficient. The species subscripts refer to the phase: (g), gas, (surf), surface, (aq), aqueous.

present, however, we will include it as a bulk aqueous phase reaction with the rate given by Park and Lee (1988). The rates of gas–surface reactions are put in as sticking coefficients, with all of these equal to 1 except that for the N_2O_4 + water reaction, which was varied from 1 to 10^{-3}, and 0 to "turn off" the heterogeneous chemistry. The surface–bulk reactions are put in as diffusion limited. Fifteen gas-phase species are included, as well as four surface species and six bulk species. The program tracks the concentration of each species in the plume, as well as the temperature, density, particle radius, surface to volume ratio, liquid volume fraction, and time. For our conditions, the program runs in less than 15 min on an IBM RISC System/6000 workstation.

RESULTS AND DISCUSSION

The results of a typical run are shown in Fig. 2. For this run, the conditions were as follows: wind speed = 10 km h^{-1}; source strength = 200 kg of N_2O_4 per minute, with 1% helium included as a reference; Gaussian plume dispersion corresponds roughly to Pasquill stability class "C", pressure = 1 atm; temperature = 293 K; background NO_2 = 20 ppb; background aerosol = 0.2 ppbv of sodium chloride aerosol, 0.5 μm in diameter; water vapor in accordance with the relative humidity, which is 95% in Fig. 2; and sticking coefficient of $N_2O_4 = 1$.

It can be seen in the figure that the volume of aerosol reaches a maximum at about 5 s downstream of the release, and most of the chemical reactions take place between 2 and 30 s downstream. Depletion of the atmospheric water vapor and a temperature rise may be seen for a brief period around 5 s. After this time, mixing of the ambient air restores the humidity and evaporates the aerosol. Note that the acid concentration within the droplets falls as the plume dilutes even though the droplets are evaporating. We also note that in spite of the temperature rise, at no time does the cloud become lighter than the surrounding air.
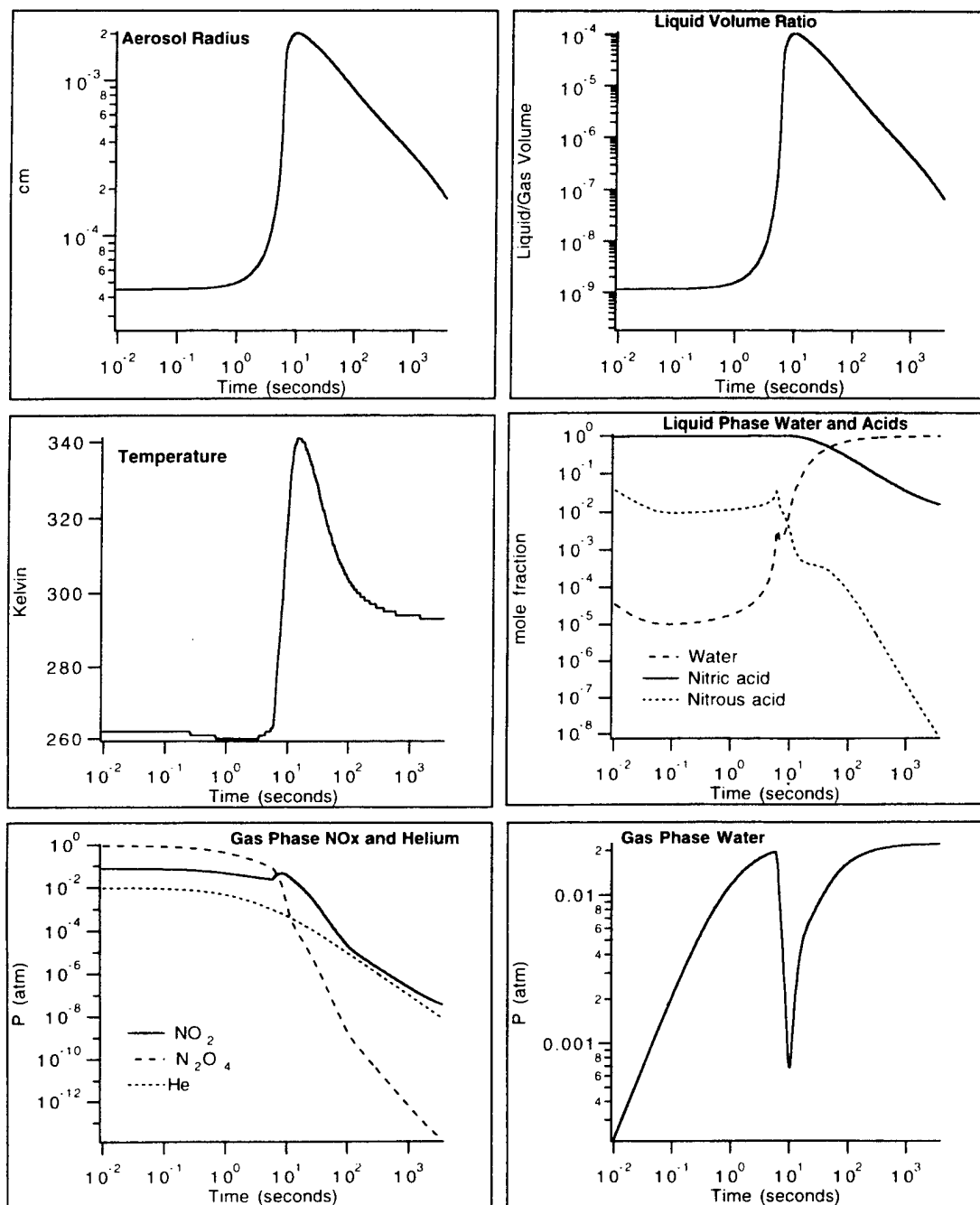
Adiabatic Parcel Evolution

Fig. 2. Time evolution of a parcel of the plume with average properties. The time base is logarithmic. Properties shown are: aerosol radius; liquid:gas volume ratio (logarithmic); temperature (linear); liquid-phase (i.e. within aerosol droplet) concentration of water, nitric acid, and nitrous acid; gas phase NO_2, N_2O_4 and He; gas-phase water (all logarithmic ordinates).

In order to observe the effects of humidity, we ran the same simulation at 95, 80, 65, 50, 30, 20, and 10% initial relative humidity. The gas-phase water concentration is the vapor pressure of pure water at 293 K times the relative humidity. The peak temperature and liquid volume, and the final gas phase NO_2 pressure and liquid mole fraction of water are plotted in Fig. 3 as a function of humidity. The peak
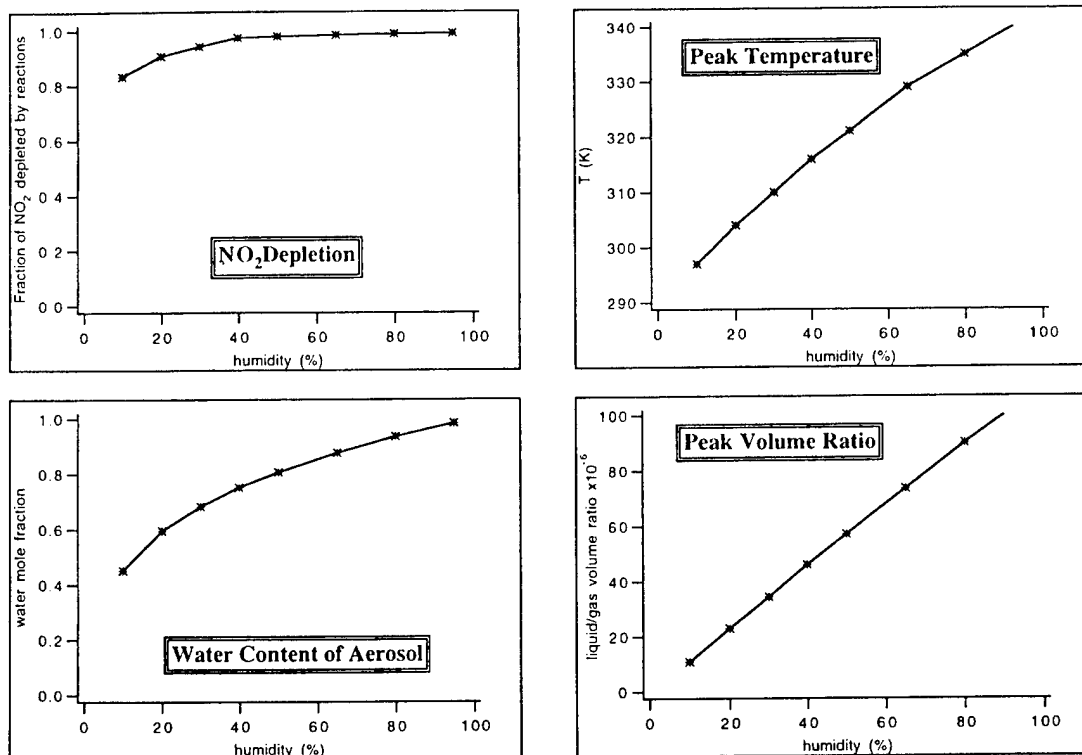
Humidity dependence of Model

Fig. 3. Summary of runs with differing initial relative humidity. Shown are fraction of NO_2 removed by aerosol chemistry; peak temperature rise; water content of aerosol after 1 h; and peak liquid:gas volume ratio. Sticking coefficient of N_2O_4 is unity.
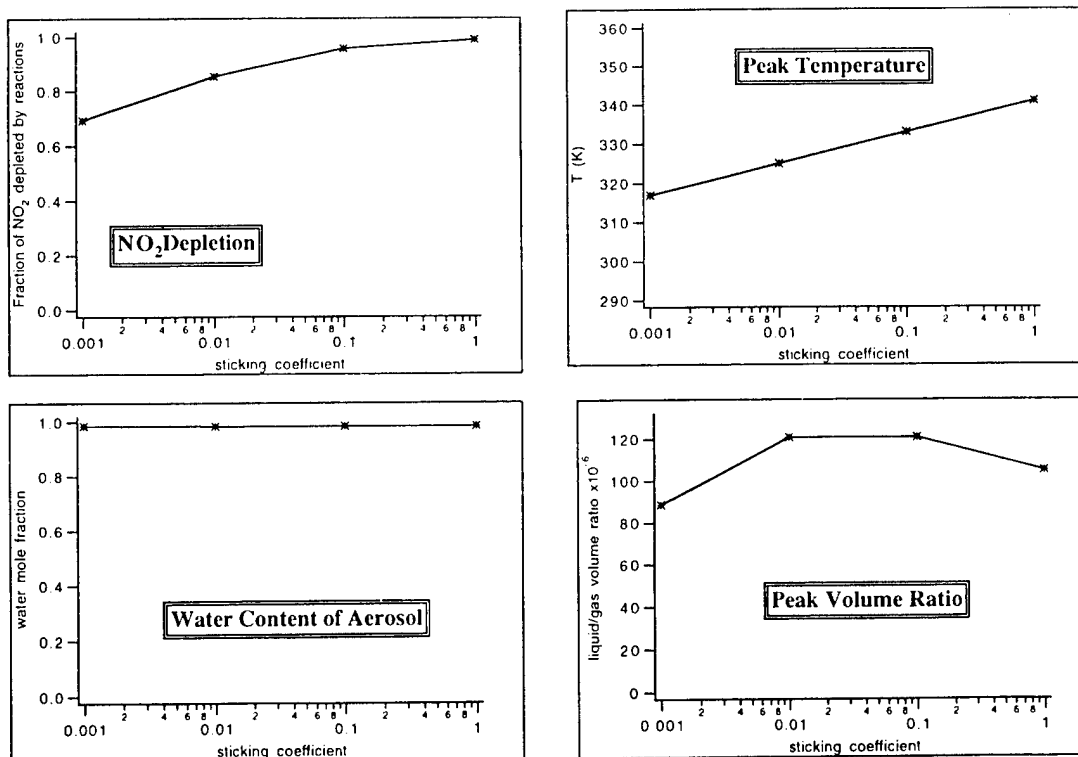

Dependence on Sticking Coefficient

Fig. 4. Summary of runs with differing values of the sticking coefficient of N_2O_4 on liquid water. Same properties are shown as in Fig. 3. Initial relative humidity is 95%.

temperature and liquid volume increase linearly with humidity, whereas the final $NO_{2(g)}$ and water concentrations asymptotically approach a limit. At 10% humidity we already see 80% conversion of the nitrogen oxides to nitric acid, and this rises to 98% at

a relative humidity of 95% (after correcting for the background NO_2).

We also investigated the effect of the surface reaction of N_2O_4 by varying the sticking coefficient from one to zero. The results are plotted on a semi-log
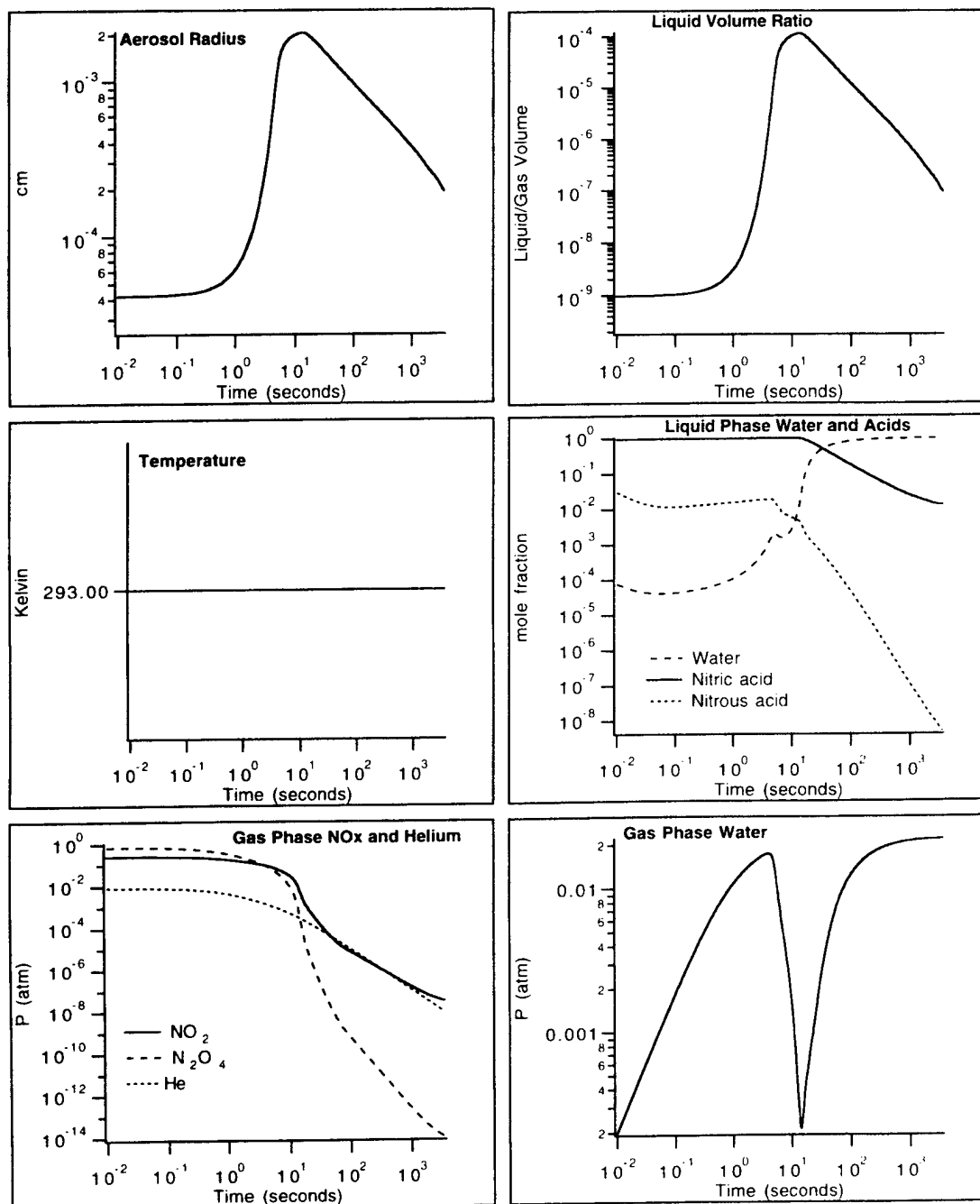
Isothermal Parcel Evolution

Fig. 5. The results of an isothermal run. An isothermal situation is not realistic for a dense spill such as this, but it illustrates the effects of heat on the plume evolution. See text for discussion.
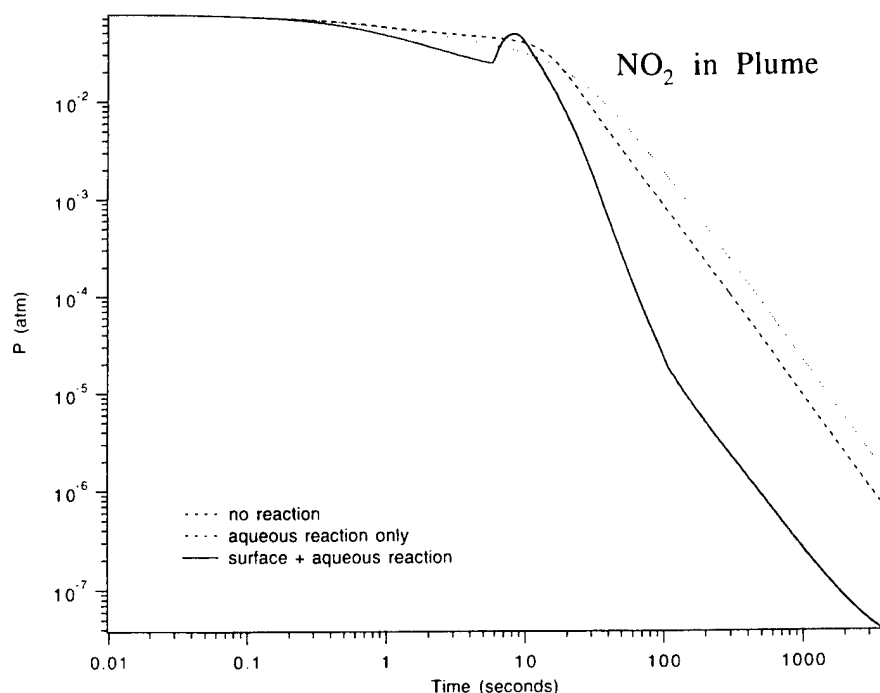
Fig. 6. This log–log plot shows the NO_2 concentration as a function of time with and without aerosol chemistry. The surface reaction of N_2O_4 is turned off by setting the sticking coefficient to zero. Aqueous reactions are turned off by setting the rates to zero.

scale in Fig. 4. The water content of the aerosol is insensitive to the sticking coefficient. The amount of conversion to nitric acid is very sensitive to this parameter, but a comparatively large number (10^{-3} or higher) seems likely in view of earlier studies (England and Corcoran, 1974). The other relationships are more complex.

The effect of adiabatic modeling can be seen in Fig. 5, which presents the results for an isothermal situation for comparison. An isothermal situation is not physically realistic for a concentrated spill, but the comparison gives insight into the effect of heat. Interestingly, there is not a great difference in the amount of final conversion of nitrogen oxides to nitric acid. These results were initially surprising to us, since we anticipated that the temperature increase due to reaction and condensation would greatly reduce the amount of aerosol chemistry. The comparatively small effect on the outcome from including adiabatic effects appears to be due to the initial temperature *decrease* resulting from the evaporation and dissociation of the N_2O_4. This initial decrease in temperature, which is ignored in the isothermal treatment, causes less dissociation of the N_2O_4 to NO_2, and consequently a more rapid initial reaction of the N_2O_4 with the aerosol. Thus, the initial fall in temperature offsets the subsequent rise in temperature.
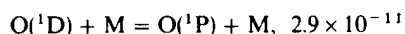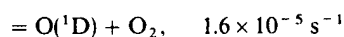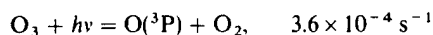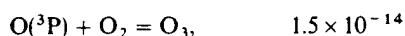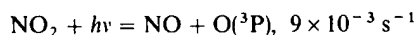
Figure 6 compares the results with and without aqueous (bulk) and surface chemistry, i.e. with and without the effect of aerosol chemistry. According to the model, inclusion of the aerosol chemistry reduces

the amount of gas phase NO_2/N_2O_4 by about a factor of ten. (This ratio decreases after about an hour due to mixing in of fresh background NO_2.) The balance is converted to nitric acid which will partly rain out as liquid, and partly evaporate into the gas phase.

SECONDARY CHEMISTRY IN THE PLUME

In a separate set of computer runs, we included an expanded set of reactions designed to mimic the essential chemistry leading to the formation of ozone and OH radicals. The reason for our interest in this chemistry is that if there were a substantial increase in the concentration of OH radicals, then there would be an increased oxidation rate of hydrocarbons and other carbon containing molecules, which would lead in turn to increased formation of peroxyacetyl nitrate (PAN). PAN is an important nitrogen containing species in urban air pollution.

The reaction set added to the basic model is as follows (k's are effective second-order rates, cm^3 molecule^{-1}s^{-1}):

$$NO_2 + hv = NO + O(^3P), \quad 9 \times 10^{-3}\,s^{-1}$$

$$O(^3P) + O_2 = O_3, \qquad\quad 1.5 \times 10^{-14}$$

$$O_3 + hv = O(^3P) + O_2, \quad 3.6 \times 10^{-4}\,s^{-1}$$

$$\qquad\quad = O(^1D) + O_2, \quad 1.6 \times 10^{-5}\,s^{-1}$$
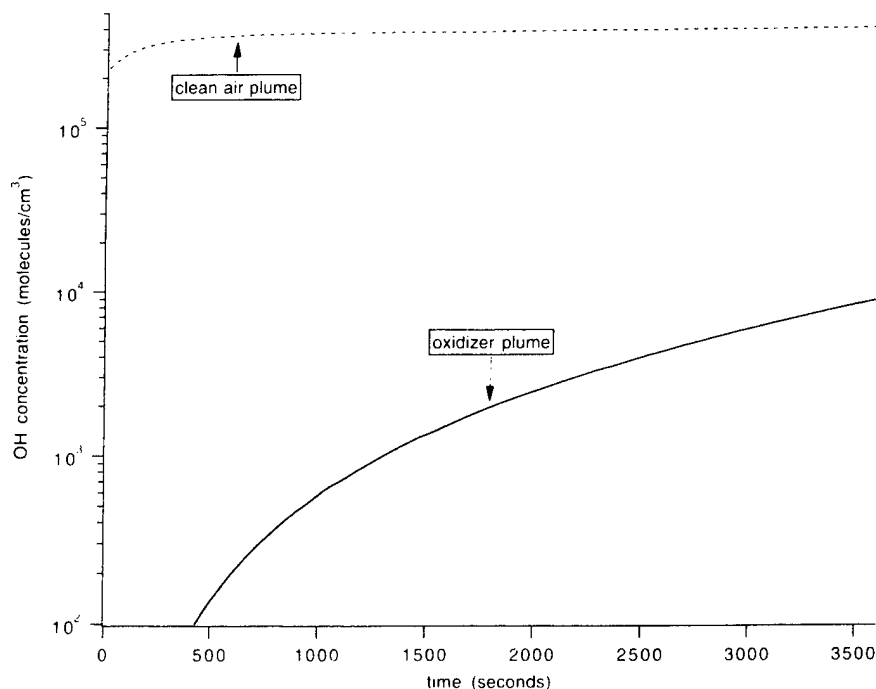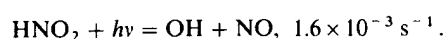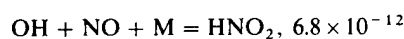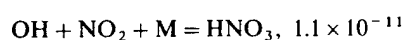
$$O(^1D) + M = O(^1P) + M, \quad 2.9 \times 10^{-11}$$

Fig. 7. This plot depicts the effect of the NO_x plume on OH concentrations. OH concentration is plotted on a log scale vs time on a linear scale for two scenarios: release of a plume of N_2O_4, and release of a plume with the same composition as the ambient air. The OH in the oxidizer plume is suppressed by two orders of magnitude. This suggests that within the 1 h time period covered by the model, hydrocarbon oxidation, and therefore, PAN formation, are not significant. At longer times the OH should recover, leading to PAN formation.

$$O(^1D) + H_2O = 2OH, \qquad 2.2 \times 10^{-10}$$

$$OH + NO_2 + M = HNO_3, \quad 1.1 \times 10^{-11}$$

$$OH + NO + M = HNO_2, \quad 6.8 \times 10^{-12}$$

$$HNO_2 + hv = OH + NO, \quad 1.6 \times 10^{-3} \, s^{-1}.$$

The results of adding this reaction set to the plume model were that the ambient ozone and OH concentrations are deeply reduced. Figure 7 shows the effect of the plume on OH concentration for full sunlight penetration, which gives an upper limit to the effect of photochemistry. Since the OH concentration is reduced by a factor of over 100 during the modeling period (1 h), there will be little oxidation of hydrocarbons and therefore little production of PAN. At longer times the OH concentration will recover, and there will be an increase in PAN due to the increased NO_x.

CONCLUSIONS

We have shown that the computer software SURFACE CHEMKIN can be adapted for modeling atmospheric aerosol chemistry, in particular the situation of a nitrogen tetroxide spill. The model here

includes the effects of heat release, formation and evaporation of an aerosol, and gas, liquid, and surface chemistry. The results are sensitive to a reaction not studied in the literature, namely, the surface reaction of the gas-phase molecule N_2O_4 with water at the aerosol surface. The results suggest that an aerosol will form over a wide range of humidities (10–95%) and that the resulting chemistry will convert roughly 90% of the nitrogen oxides to nitric acid.

This model uses a simplistic dispersion model but treats the multiphase chemistry rigorously. If a more accurate dispersion model were included it could provide an even better picture of the plume dynamics, but such a model would be computationally intensive. In the chemical system treated here, the unique aerosol chemistry is over very quickly. This suggests that the chemical make-up of the plume at 100 s calculated using SURFACE CHEMKIN could be used as the source term in a more precise dispersion model. This would give a more accurate concentration downstream for reasonable computation times.

more for supplying the SURFACE CHEMKIN program material.

REFERENCES

Balentine H. W. and Eltgroth M. W. (1985) Validation of a horizontal spill model using N_2O_4 spill data. *Proc. APCA Annu. Meet.*, 78th (Vol. 2), 85-25B.1, 11 pp.

Brasseur G. P., Granier C. and Walters S. (1990) Future changes in stratospheric ozone and the role of heterogeneous chemistry. *Nature* **348**, 626-628.

Chase M. W. Jr., Davies C. A., Downey J R. Jr., Frurip D. J., McDonald R. A. and Syverud A. N. (1985) JANAF Thermochemical Tables Third Edition. *J. Phys. Chem. Ref. Data* **14** (Suppl. 1), 1856 pp.

Cho S. Y., Yetter R. A. and Dryer F. L. (1992) A computer model for one-dimensional mass and energy transport in and around chemically reacting particles, including complex gas-phase chemistry, multicomponent molecular diffusion, surface evaporation, and heterogeneous reaction. *J. Comp. Phys.* **102**, 160-179.

Coltrin M. E., Kee R. J. and Rupley F. M. (1991) SURFACE CHEMKIN (Version 4.0): a Fortran package for analyzing heterogeneous chemical kinetics at a solid-surface-gas-phase interface, Sandia Report SAND90-8003B.UC-401, 91 pp.

Corbett J. O. (1981) The validity of source-depletion and alternative approximation methods for a Gaussian plume subject to dry deposition. *Atmospheric Environment* **15**, 1207-1213.

Daum P. H., Kelly T. J., Schwartz S. E. and Newman L. (1984) Measurements of the chemical composition of stratoform clouds. *Atmospheric Environment* **18**, 2671-2684.

England C. and Corcoran W. H. (1974) Kinetics and mechanism of the gas-phase reaction of water vapor and nitrogen dioxide. *Ind. Engng Chem. Fundam.* **13**, 373-384.

Granier C. and Brasseur G. (1992) Impact of heterogeneous chemistry on model predictions of ozone changes. *J. geophys. Res.* **97**, 18,015-18,033.

Haas W. R. and Prince S. (1984) Atmospheric dispersion of hypergolic liquid rocket fuels (Volume I of II), Report, AFESC/ESL-TR-84-18, 31 pp.

Heikes B. G. and Thompson A. M. (1983) Effects of heterogeneous processes on NO_3, HONO, and HNO_3 chemistry in the troposphere. *J. geophys. Res.* **88**, 10,883-10,895.

Horst T. W. (1977) A surface depletion model for deposition from a Gaussian plume. *Atmospheric Environment* **11**, 41-46.

Huebert B. J. and Robert C. H. (1985) The dry deposition of nitric acid to grass. *J. geophys. Res.* **90**, 2085.

Kee R. J., Rupley F. M. and Miller J. A. (1991a) The Chemkin Thermodynamic Data Base, Sandia Report SAND87-8215B.UC-4, 155 pp.

Kee R. J., Rupley F. M. and Miller J. A. (1991b) Chemkin-II: a fortran chemical kinetics package for the analysis of gas-phase chemical kinetics, Sandia Report SAND89-8009.UC-401, 127 pp.

Kobayashi H., Takezawa N., Hara K., Niki T. and Kitano K. (1976) The mechanism of nitrous acid decomposition. *Nippon Kagaku Kaishi* **3**, 383-387.

Kunkel B. A. (1992) A review and evaluation of the ADAM 2.1 dispersion model, PL-TR-92-2245. Environmental Research Papers, No. 1109 Phillips Laboratory, Hanscom Air Force Base, Massachusetts, 68 pp.

Levine S. Z. and Schwartz S. (1982) In-cloud and below-cloud scavenging of nitric acid vapor. *Atmospheric Environment* **16**, 1725-1734.

Lyons W. A., Moon D. A., Eastman J. L., Keen C. S., Venne M. G., Pielke R. A., Cotton W. R., Walko R. L. and Tremback C. J. (1990) *Proc. 83rd Ann. Mtg Air and Waste Management Assn.* 90-79.5, pp. 2-16.

Martin L. R. (1984) Kinetic studies of sulfite oxidation in aqueous solution. In SO_2, NO and NO_2 *Oxidation Mechanisms: Atmospheric Considerations* (edited by Calvert J. G.), pp. 63-100. Butterworth, Boston.

McElroy M. B. and Salawitch R. J. (1989) Changing composition of global stratosphere. *Science* **243**, 763-770.

McElroy M. B., Salawitch R. J. and Wofsy S. C. (1986) Antarctic O_3: chemical mechanisms for the spring decrease. *Geophys. Res. Lett.* **13**, 1296-1299.

McRae T. G. (1985) Analysis and model/data comparisons of large-scale release of nitrogen tetroxide, Lawrence Livermore National Laboratory Report UCID-20388, 78 pp.

McRae G. J. and Russell A. G. (1984) Dry deposition of nitrogen containing species. In *Deposition both Wet and Dry* (edited by Hicks B. B.), Chap. 9, pp. 153-193, Acid Precipitation Series, J. I. Teasley, Series Ed. Butterworth, Boston.

McRae T. G., Goldwire H. C. Jr. and Koopman R. P. (1984) The evaporation and gaseous dispersion of large-scale release of nitrogen tetroxide, Lawrence Livermore National Laboratory Report UCRL-89687, 22 pp.

McRae T. G., Cederwall R. T., Ermak D. L., Goldwire H. C. Jr., Hipple D. L., Johnson G. W., Koopman R. P., McClure J. W. and Morris L. K. (1987) Eagle Series Data Report: 1983 Nitrogen Tetroxide, Lawrence Livermore National Laboratory Report UCID-20063-Rev.1, 141 pp.

Moller D. and Mauersberger G. (1992) Cloud chemistry effects on tropospheric photooxidants in polluted atmosphere—model results. *J. atmos. Chem.* **14**, 153-165.

Mullett C. A. and Raj P. K. (1990) A User's Manual for ADAM GL-TR-90-0321(II), Geophysics Laboratory, Hanscom Air Force Base, Massachusetts, 60 pp.

National Research Council (1928) *International Critical Tables of Numerical Data, Physics, Chemistry and Technology* (edited by Washburn E. W.), Vol. III, pp. 304-305. McGraw-Hill, New York.

NIST Chemical Kinetics Database Version 4.0 (1992) U.S. Department of Commerce National Institute of Standards and Technology, Standard Reference Data Program, Gaithersburg, Maryland.

Oppenheimer M. (1983) The relationship of sulfur emissions to sulfate in precipitation. *Atmospheric Environment* **17**, 451-460.

Overcamp T. J. (1976) A general Gaussian diffusion-depletion model for elevated point sources. *J. Appl. Meteorology* **15**, 1167-1171.

Park J.-Y. and Lee Y.-N. (1988) Solubility and decomposition kinetics of nitrous acid in aqueous solution. *J. Phys. Chem.* **92**, 6294-6302.

Pilinis C., Pandis S. N. and Seinfeld J. H. (1992) Aerosol scavenging and processing in fogs. In *Precip. Scavenging Atmos.-Surf. Exch.*, Vol. 1 [*Proc. Int. Conf.*], 5th 1991 (pub. 1992) (edited by Schwartz S. E. and Slinn W. G. N.), pp. 271-282.

Raj P. K. and Morris J. A. (1987) Source characterization and heavy gas dispersion models for reactive chemicals AFGL-TR-88-0003(I), Air Force Geophysics Laboratory, Hanscom Air Force Base, Massachusetts, 258 pp.

Rodean H. C. (1989) Toward more realistic material models for release and dispersion of heavy gases, Lawrence Livermore National Laboratory Report DE90-012015, 39 pp.

Rodean H. C. (1991) A structure for models of hazardous materials with complex behavior. *Atmospheric Environment* **25A**, 885-898.

Schwartz S. (1984) Gas-aqueous reactions of sulfur and nitrogen oxides in liquid-water clouds. In SO_2, NO and NO_2 *Oxidation Mechanisms: Atmospheric Considerations* (edited by Calvert J. G.), pp. 173-208. Butterworth, Boston.

Solomon S., Garcia R. R., Rowland F. S. and Wuebbles D. J. (1986) On the depletion of Antarctic ozone. *Nature* **321**, 755-758.

Spicer T. O. and Havens J. A. (1987) Field test validation of the degadis model. *J. Hazardous Mater.* **16,** 231–245.

Spicer T. O., Havens J. A., Tebeau P. A. and Key L. E. (1986) Degadis—a heavier-than-air atmospheric dispersion model, *Proc. APCA Annu. Meet.,* 78th (Vol. 2), 86/42.2, 35 pp.

Watje W. F. (1978) Potential of a nitrogen tetroxide spill or emission during movement from supplier to user, *Proceedings of the NASA/Florida Institute of Technology Environmental Engineering Conference on Nitrogen Tetroxide* (NASA), Melbourne, Florida, March 1978. NASA Conference Publication 2049 Paper N79-20426, pp. 11–22.